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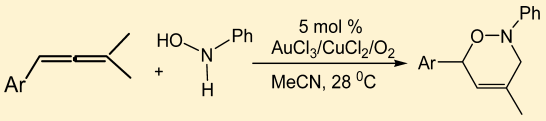
Catalytic Formal [4 + 2] Cycloadditions between Unactivated Allenes and *N*-Hydroxyaniline Catalyzed by $AuCl_3/CuCl_2/O_2$

Jian-Ming Chen, Chin-Jung Chang, Yao-Jin Ke, and Rai-Shung Liu*

Department of Chemistry, National Tsing Hua University, Hsinchu, Taiwan, ROC

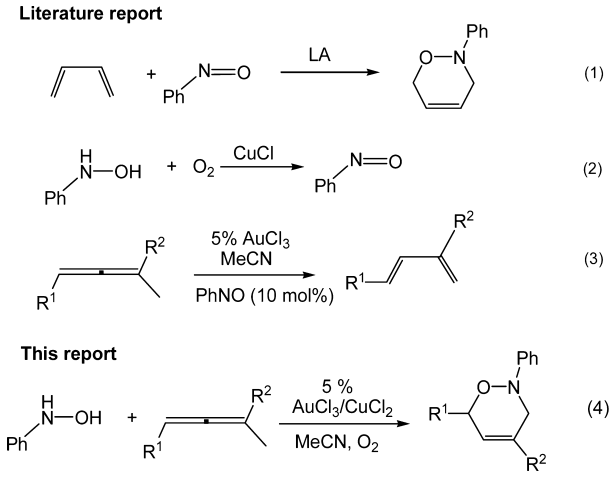
Supporting Information

ABSTRACT: $AuCl_3$-catalyzed formal [4 + 2]-cycloadditions between substituted allenes and *N*-hydroxyanilines are described. This reaction sequence comprises initial isomerizations of allenes to butadienes under N_2 and subsequent oxidations of *N*-hydroxyanilines to nitrosoarenes under O_2. $CuCl_2$ (5 mol %) was added in the second step to increase the oxidation efficiency. The reactions are compatible with various 1,1-di- and 1,1,3-trisubstituted allenes and *N*-hydroxyaniline derivatives. Our experimental data reveal that the roles of $AuCl_3$ are 3-fold, including catalytic oxidations of *N*-hydroxyaniline derivatives to nitrosoarenes, isomerizations of alkyl-substituted allenes to dienes, and final nitroso/butadiene [4 + 2] cycloadditions.



INTRODUCTION

Lewis acid catalyzed [4 + 2] cycloadditions of butadienes with nitroso species are useful tools to access highly functionalized molecules because both nitrogen and oxygen functionalities are introduced at the 1,4-carbons of the product skeletons (eq 1);



the resulting N−O bond of products is readily cleaved with chemical reduction.[1,2] High regio- and enantioselectivity of these [4 + 2] cycloaddition have been implemented with suitable chiral acid catalysts.[1,2] Nitrosoarenes are generally prepared from the oxidation of *N*-hydroxyanilines with suitable oxidants.[1a,3] Among the reported methods, the use of copper catalysts and oxygen[3e,f,4] is particularly appealing because of the low cost. Development of Cu-catalyzed cascade [4 + 2] cycloadditions between *N*-hydroxyanilines and dienes was reported by de Alaniz.[4]

Recently, we reported gold-catalyzed room-temperature isomerizations of unactivated allenes to butadienes in CH_3CN with nitrosobenzene as an additive (a proton shuttle);[5] subsequent [4 + 2] cycloadditions between the resulting dienes and nitrosobenzene proceeded rather slowly in the presence of $AuCl_3$. Interest in gold catalysis stimulates new cascade reactions because gold complexes can initiate electrophilic activations of various functional groups including alkynes, allenes, alkenes, epoxides and carbonyls.[6] Furthermore, many gold complexes can tolerate other metal catalysts and organocatalysts, thus allowing the combination of two individual steps into one-pot operations.[7] In this work, we report new formal [4 + 2] cycloadditions between unactivated allenes and *N*-hydroxyanilines, as described in eq 4; this cascade sequence merges three separate steps (eqs 1−3) into a single process. Of particular interest is the use of $AuCl_3$ to catalyze all three steps in this sequence; herein, $CuCl_2$ additive is added to enhance the oxidation of *N*-hydroxyaniline to nitrosobenzene. Catalytic air oxidation of *N*-hydroxyaniline to nitrosobenzene and $AuCl_3$-catalyzed nitroso/diene cycloaddition remain unclear in gold catalysis.

RESULTS AND DISCUSSION

Shown in Table 1 is the realization of a new formal [4 + 2] cycloaddition between allene **1a** and *N*-hydroxyaniline in CH_3CN at room temperature (rt). We sought suitable catalysts to realize this whole sequence with oxygen as the oxidant. We tested the reaction with $AuCl_3$ (5 mol %) because of its high activity in the isomerization of unactivated allenes to butadienes at rt (eq 3).[5] As shown in entry 1, an initial treatment of allene **1a** with *N*-hydroxyaniline in CH_3CN (28 °C, 3 h) under N_2 resulted in a clean isomerization to butadiene **2a**; this CH_3CN solution was charged with an oxygen balloon before a slow addition of *N*-hydroxyaniline (3 equiv) in MeCN. A workup afforded 3,6-dihydro-2*H*-1,2-oxazine **3a** in 75% yield. When the entire sequence was performed under N_2, the yield of desired

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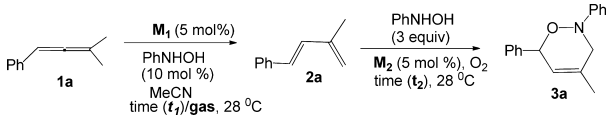
Table 1. Formal [4 + 2]-Cycloadditions over Various Catalysts



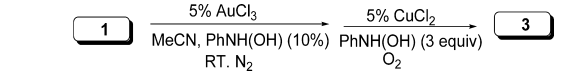
						compd (yield, %)[b]		
entry	M_1	M_2	gas	t_1 (h)	t_2 (h)	1a	2a	3a
1	$AuCl_3$		N_2	3	24	0	0	75 (22)[d]
2	$AuCl_3$		O_2	5	24	0	0	54
3	$AuCl_3$[c]		O_2	48		70	0	0
4	$AuBr_3$		N_2	14	48	0	0	49
5	$PicAuCl_2$		N_2	48	60	0	0	45
6	AuCl		N_2	48		76	0	0
7	LAuCl/ $AgNTf_2$		N_2	72		67	0	0
8	$CuCl_2$		N_2	48		81	0	0
9	$AuCl_3$		N_2	3		0	91	0
10	$AuCl_3$		O_2	5		0	85	0
11	$AuCl_3$	$CuCl_2$	N_2	3	18	0	0	87
12	$AuCl_3$	$CuBr_2$	N_2	3	15	0	0	78

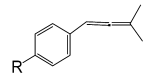
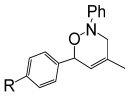
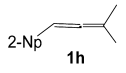
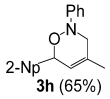
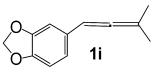
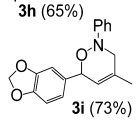
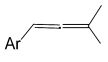
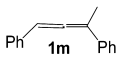
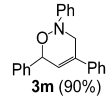
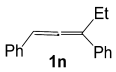
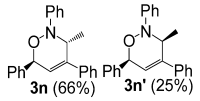
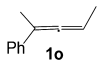
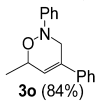
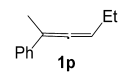
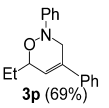
[a][1a] = 0.1 M, **L** = PPh_3, 0_2 (1 atm). [b]Yields are reported after purification from a silica column. [c]In entry 3, PhNHOH (3.1 equiv) was used to test a one-step operation. [d]This value corresponds to N_2, which replaces O_2 in the cycloaddition.

cycloadduct **3a** was only 22% (entry 1). When the allene → diene (**1a** → **2a**) transformation was performed under O_2 (entry 2), desired cycloadduct **3a** was obtained in 54% yield. Entry 3 shows a one-step operation involving $AuCl_3$ (5 mol %), allene (**1a**), and PhNHOH (3.1 equiv) in MeCN and under O_2; this mixture gave only unreacted **1a** in 70% recovery. Excessive PhNHOH reduces the acidity of $AuCl_3$, thus inhibiting the allene → diene isomerization. With a standard procedure in entry 1, $AuBr_3$ and $PicAuCl_2$ became less efficient to form cycloadduct **3a** in 49% and 45% yields, respectively (entries 4 and 5). We performed the initial isomerization of **1a** with AuCl under N_2 atmosphere, and starting **1a** was recovered in 76% yield (entry 6). Commonly used $PPh_3AuCl/AgNTf_2$ and $CuCl_2$ failed to give the desired product **3a** in a tractable proportion because of their inactivity in the initial **1a** → **2a** isomerization (entries 7 and 8). Entries 9 and 10 suggested that *N*-hydroxyaniline was also an effective additive in the **1a** → **2a** isomerization because of a shorter period and a better yield of diene **2a** (3 h)[8] under N_2; nitrosobenzene was found to be more abundant in the presence of oxygen (see Table 4, entries 3 and 4; vide infra). We added $CuCl_2$ and $CuBr_2$ in the second step to increase the oxidation efficiency of *N*-hydroxyaniline to nitrosobenzene[1a,3] (entries 11 and 12), and the yields of desired **3a** were increased to 87% and 78%, respectively. The structure of cycloadduct **3a** was confirmed by its ^1H NOE; the two singlets in the δ 5−6 ppm were assignable to the OPhC*H*−C*H*= protons, and the PhN−CH_2 protons appear as AB quartets at δ 3.75 ppm. Such a regioselectivity is consistent with literature reports.[9,10]

To assess the reaction scope, we examined the cycloadditions of various trisubstituted allenes **1b**−**p** with *N*-hydroxyanilines; the results are summarized in Table 2. The catalytic reaction was operated according to the procedure described in Table 1 (entry 11). We investigated the effect of various phenyl substituents (R = Cl, F, Br, CF_3, Me, and OMe) as in allenes

Table 2. Substrate Scope of formal [4 + 2]-Cycloadditions



	allenes	t_1 (hour)	t_2 (hour)	Products
				
(1)	R = Cl (**1b**)[a]	6	24	**3b** (81%)[b]
(2)	R = F (**1c**)	4	23	**3c** (87%)
(3)	R = Br (**1d**)	6	18	**3d** (78%)
(4)	R = CF_3 (**1e**)	48	48	**3e** (60%)
(5)	R = Me(**1f**)	1.5	20	**3f** (84%)
(6)	R = OMe(**1g**)	1.5	20	**3g** (72%)
(7)	 **1h**	2	24	 **3h** (65%)
(8)	 **1i**	0.5	16	 **3i** (73%)
				
(9)	Ar = 3-furanyl (**1j**)	1	20	**3j** (67%)
(10)	Ar = 2-furanyl (**1k**)	1	18	**3k** (69%)
(11)	Ar = 2-thienyl (**1l**)	1	18	**3l** (67%)
(12)	 **1m**	1	8	 **3m** (90%)
(13)	 **1n**	1	12	 **3n** (66%) **3n'** (25%)
(14)	 **1o**			 **3o** (84%)
(15)	 **1p**	2	16	 **3p** (69%)

[a][1] = 0.1 M. [b]Product yields are reported after separation from a silica column.

1b−**g** (entries 1−6); their corresponding products **3b**−**g** were obtained with yields exceeding 72% in most instances except trifluoromethyl derivative **3e** that was produced in 60% yield (entry 4). In the **1** → **2** isomerization, short reaction periods (t_1) of electron-rich allenes **1f** and **1g** were consistent with our previous observations.[5] For 2-naphthyl- and 1,3-benzodioxolyl-substituted allenes **1h** and **1i**, their resulting cycloadducts **3h** and **3i** were obtained in 65% and 73% yields, respectively (entries 7 and 8). These gold-catalyzed cascade reactions were compatible with heteroaryl-substituted allenes **1j**−**l** (Ar = 2- or 3-furanyl and 2-thienyl), affording desired the cycloadducts **3j**−**l** in satisfactory yields (67−69%, entries 9−11). Entries 12 and 13 showed the cycloadditions of trisubstituted allenes **1m** and **1n** bearing two phenyl groups at the 1- and 3-allenyl carbons respectively, producing desired cycloadducts **3m** and **3n** in 90−91% yields. For allene **1n**, two diastereomeric cycloadducts **3n**

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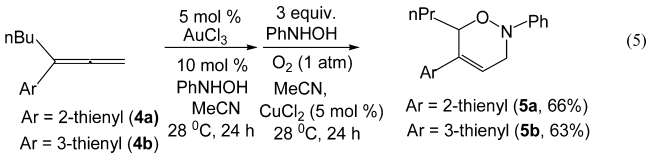
and **3n′** were produced and separable on a silica column; the structure of compound **3n** was confirmed by X-ray diffraction.[11] The reactions were extendible to trisubsituted allenes **1o** and **1p** bearing two alkyl groups at the 1- and 3-allenyl carbons, affording desired cycloadducts **3o** and **3p** in 84% and 69% yields, respectively (entries 14 and 15); herein, the *Me*PhC═ methyl group was preferably functionalized, whereas the other methyl or ethyl groups remained intact.

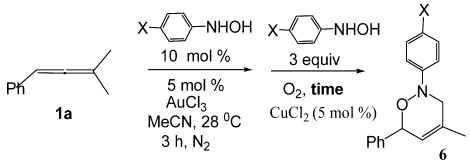
We prepared 1,1-disubstituted allenes **4a** and **4b** to test their catalytic reactions with *N*-hydroxyaniline, giving the desired [4 + 2]-cycloadducts **5a** and **5b** in 66% and 63% yields, respectively (eq 5). We examined the reactions also on



(5)

substituted *N*-hydroxyanilines to expand the reaction scope. As shown in Table 3, these new oxidative cycloadditions were

Table 3. [4 + 2]-Cycloadditions with Various *N*-Hydroxyanilines



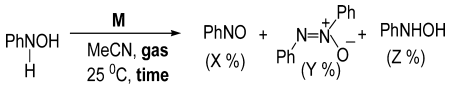
entry	*N*-hydroxyaniline X	time (h)	compd (yield, %)
1	Me	32	**6a** (71)
2	*t*-Bu	30	**6b** (73)
3	Cl	40	**6c** (81)
4	F	44	**6d** (69)

[a][**1a**] = 0.1 M. [b]Product yields are reported after separation from a silica column.

extendible to several *N*-hydroxyanilines bearing alterable *p*-phenyl substitutents X = methyl, *tert*-butyl, chloro, and fluoro, affording desired cycloadducts **6a**–**d** in 69–81% yields.

Table 4 shows the control experiments to elucidate the oxidation behavior of *N*-hydroxyaniline affected by $AuCl_3$ (5 mol %); the product distributions are estimated by ^1H NMR. In the absence of $AuCl_3$, the oxidation of *N*-hydroxyaniline to

Table 4. Effects of Catalysts and Gas on *N*-Hydroxyaniline

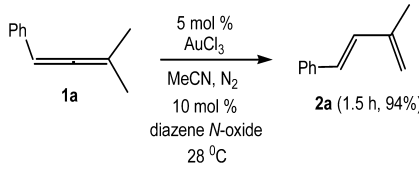


entry	M[a,b] (mol %)	gas	time (h)	*X*	*Y*	*Z*
1		O_2	24	0	13	74
2		N_2	24	0	7.5	85
3	$AuCl_3$ (1.7)	O_2	24	27	5	63
4	$AuCl_3$ (1.7)	N_2	24	13	11.5	67
5	$AuCl_3$ (1.7)/$CuCl_2$ (1.7)	O_2	24	48	16	20
6	$AuCl_3$ (50)	O_2	3	13	22	43
7	$AuCl_3$ (50)	N_2	3	3	28	41

[a][*N*-Hydroxyaniline] = 0.31 M. [b]Product yields are reported after separation from a silica column.

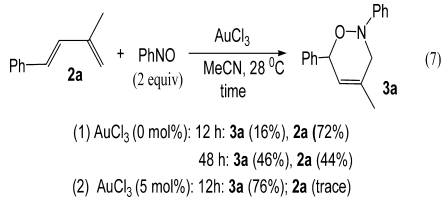
nitrosobenzene failed to proceed in acetonitrile under O_2 or N_2 (entries 1 and 2). Under O_2, $AuCl_3$ (1.7 mol %) catalyzed the transformation of *N*-hydroxyaniline into nitrosobenzene and diazene *N*-oxide in 27% and 5% yields, respectively, together with a 63% recovery of unreacted *N*-hydroxyaniline (entry 3). Under N_2, nitrosobenzene and diazene *N*-oxide were formed from $AuCl_3$ and *N*-hydroxyaniline in 13% and 11.5% yields, respectively (entry 4). If $AuCl_3$ was used at a 50% loading under O_2, nitrosobenzene and diazene *N*-oxide were produced in 3% and 13% yields, respectively. With this catalyst loading under N_2, the yield of nitrosobenzene was decreased to 3% together with an increased yield of diazene *N*-oxide (28%). Herein, $AuCl_3$ enabled a reversible redox reaction between nitrosobenzene and *N*-hydroxyaniline.[12] Furthermore, *N*-hydroxyaniline itself was known to undergo slow decomposition to form diazene *N*-oxide and aniline in solution,[13] but we were unable to detect aniline with tractable amount.

Analysis of the product distributions in Table 4 suggests that diazene *N*-oxide is probably the truly active component for the isomerization of allene to diene with PhNH(OH). We tested the reactivity of diazene *N*-oxide versus PhNH(OH) using $AuCl_3$ catalyst; the results are shown in eq 6. With diazene *N*-oxide (10 mol %) as an promoter, the isomerization of allene **1a** to diene **2a** was complete within 1.5 h with 94%, more efficient than PhNHOH (Table 1 entry 9).



(6)

We also examined the effect of $AuCl_3$ on the [4 + 2] cycloaddition between diene **2a** and nitrosobenzene; the results are shown in eq 7. The desired [4 + 2]-cycloadduct **3a** was



(7)

produced in 16% yield in the absence of $AuCl_3$ for a brief period but increased significantly to 76% yield when $AuCl_3$ was present. The catalytic role of $AuCl_3$ on the nitroso/diene cycloaddition was thus ascertained.

We also performed additional experiments to compare the efficiency between nitrosobenzene and *N*-hydroxyaniline as starting reagents; the results are provided in Table 5. No reaction occurred between *N*-hydroxyaniline and allene **1a** in acetonitrile in the absence of $AuCl_3$ (entry 1). The yield of the desired cycloadduct **3a** was decreased to 68% when DCM replaced MeCN (entry 2). If $CuCl_2$ (5 mol %) was present was present in the second step, the yield of compound **3a** was increased to 81%. Compared to data in Table 1 (entries 1 and 11), MeCN is thus better than DCM as the reaction solvent. We also performed the reactions using nitrosobenzene; the yields of desired **3a** in DCM were 87% and 82%, under N_2 or O_2 respectively. Similar yields were obtained for product **3a** if nitrosobenzene was used in MeCN. The better yields of compound **3a** from nitrosobenzene than *N*-hydroxyaniline

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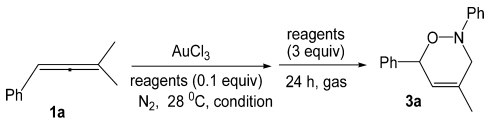
Table 5. *N*-Hydroxyaniline and Nitrosobenzene as Reagents



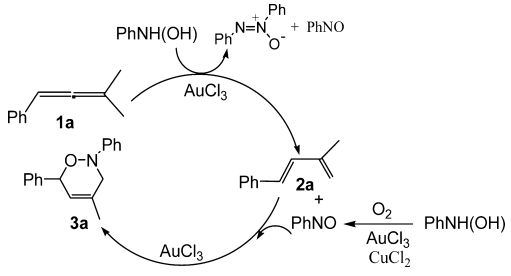
entry	$AuCl_3$ (x mol %)	reagents[a]	conditions	gas	compounds (%) 1a	3a[b]
1	0	PhNHOH	MeCN/3 h	O_2	78	
2	5	PhNHOH	DCM/3 h	O_2		68 (81%)[c]
3	5	PhNO	DCM/3 h	O_2		87
4	5	PhNO	DCM/3 h	N_2		82
5	5	PhNO	MeCN/3 h	O_2		86
6	5	PhNO	MeCN/3 h	N_2		81

[a][1a] = 0.1 M. [b]Product yields are reported after purification from a silica column. [c]The value in parentheses corresponds to added $CuCl_2$ (5 mol %) for a period of 15 h.

(Table 1, entries 1 and 2) are reasonable because an extra step is involved in the oxidation of *N*-hydroxyaniline to nitrosobenzene. But the efficiency of PhNH(OH) become comparable to that of nitrosobenzene if $CuCl_2/O_2$ is present in the second oxidation phrase.

We postulate a mechanism to rationalize a formal [4 + 2] cycloaddition between *N*-hydroxyaniline and allene **1a**. $AuCl_3$, like $CuCl_2$, was shown to catalyze the dehydrogenation of *N*-hydroxyaniline to form nitrosobenzene, as depicted in Table 4 (entries 3−7); this transformation could proceed under N_2, but more efficiently under O_2. An isomerization of allene **1a** to diene **2a** could be implemented by $AuCl_3$ and nitrosobenzene, as revealed in our previous work.[5] Under nitrogen, we observed that *N*-hydroxyaniline was also active to implement this allene → diene (**1a** → **2a**) isomerization because the yield of diene **2a** is better in the presence of N_2 than O_2 (see entries 9 and 10, Table 1). Subsequent control experiments suggests that diazene *N*-oxide was more active than PhNHOH for this isomerization.[15] $AuCl_3$ eventually proved to catalyze a cycloaddition between diene **2a** and nitrosobenzene in MeCN, as depicted in eq 6. These data supports a postulated route in Scheme 1. This

Scheme 1. Plausible Reaction Mechanism



proposed mechanism summarizes the active role of $AuCl_3$ on the three elementary steps in eqs 1−3. Among these steps, diazene *N*-oxide greatly assists the allene → diene isomerization and $CuCl_2$ enhances the efficiency of the oxidation of PhNHOH to PhNO.

CONCLUSIONS

Formal [4 + 2] cycloadditions between substituted allenes and *N*-hydroxyallenes under O_2 are implemented by $AuCl_3/CuCl_2$ catalysts. The reactions are compatible with a reasonable range of allene substrates including 1,1-di- and 1,1,3-trisubstituted allenes and *N*-hydroxyaniline derivatives. Our mechanistic analysis reveals the 3-fold roles of $AuCl_3$ including catalytic oxidations of *N*-hydroxyanilines to nitrosobenzenes, isomerizations of alkyl-substituted allenes to dienes, and final nitroso/diene [4 + 2]-cycloadditions. Herein, *N*-hydroxyaniline generates diazene *N*-oxide that turns out to be very active to implement with $AuCl_3$ in the isomerization of unactivated allenes to butadienes.

EXPERIMENTAL SECTION

General Comments. Unless otherwise noted, all reactions were performed in oven-dried glassware under N_2 with freshly distilled solvents. CH_3CN was distilled from CaH_2 under nitrogen and stored over molecular sieves (4 Å) before use. All other commercial reagents were used without further purification, unless otherwise indicated. ^1H and ^{13}C NMR spectra were recorded on 400 or 600 MHz spectrometers using chloroform-d_1 ($CDCl_3$) as internal standards. HRMS was performed on a double-focusing sector mass spectrometer in EI mode. Allene compounds (**1a−p**, **4a,b**) were prepared according to the methods reported in our previous work;[5] *N*-Phenylhydroxylamine compounds were prepared from the reductions of nitrobenzene[14] according to literature procedures;[14] newly prepared compounds were stored in darkness.

General Procedure for Gold-Catalyzed [4 + 2]-Cycloadditions between (3-Methylbuta-1,2-dien-1-yl)benzene (1a) and *N*-Hydroxyaniline. A flask (10 mL) containing $AuCl_3$ (5.3 mg, 5.0 mol %) was dried in vacuum for 1 h before it was filled with N_2 using a N_2 balloon. This flask was charged with an acetonitrile (2 mL) solution containing allene **1a** (50 mg, 0.35 mmol) and *N*-phenylhydroxylaniline (4.3 mg, 0.035 mmol); the mixture was stirred at room temperature for 3 h. The resulting solution was then flushed with O_2 and charged with a O_2 balloon. To this solution was added $CuCl_2$ (2.4 mg, 5 mmol), followed by an acetonitrile (1.5 mL) solution of *N*-phenylhydroxylaniline (129 mg, 1.05 mmol); the mixture was stirred for 6 h. The resulting solution was concentrated and eluted through a silica column (pentane) to afford compound **3a** (75.9 mg, 0.26 mmol, 87%). This procedure was applicable to other allene substrates (**1b−p** and **4a,b**) with a 50-mg scale.

*4-Methyl-2,6-diphenyl-3,6-dihydro-2H-1,2-oxazine (**3a**):* pale yellow oil (75.9 mg, 87%); ^1H NMR (400 MHz, $CDCl_3$) δ 7.42 (d, J = 8.4 Hz, 2 H), 7.35−7.22 (m, 5 H), 7.08 (d, J = 8.4 Hz, 2 H), 6.93 (t, J = 6.8 Hz, 1 H), 5.73 (s, 1 H), 5.51 (s, 1 H), 3.75 (AB quartets, J = 7.2 Hz, 2 H), 1.87 (s, 3 H); ^{13}C NMR (100 MHz $CDCl_3$) δ 150.2, 139.5, 131.5, 128.7, 128.4, 128.2, 128.0, 122.9, 122.1, 115.8, 79.3, 55.3, 20.3; HRMS calcd for $C_{17}H_{17}NO$ 251.1310, found 251.1308.

*6-(4-Chlorophenyl)-4-methyl-2-phenyl-3,6-dihydro-2H-1,2-oxazine (**3b**):* pale yellow oil (65.0 mg, 81%); ^1H NMR (400 MHz, $CDCl_3$) δ 7.38 (d, J = 8.4 Hz, 2 H), 7.32 (d, J = 8.4 Hz, 2 H), 7.28 (t, J = 7.6 Hz, 2 H), 7.08 (d, J = 7.6 Hz, 2 H), 6.97 (t, J = 6.8 Hz, 1 H), 5.70 (s, 1 H), 5.47 (s, 1 H), 3.75 (AB quartets, J = 7.2 Hz, 2 H), 1.88 (s, 3 H); ^{13}C NMR (100 MHz $CDCl_3$) δ 150.1, 138.1, 134.0, 132.0, 129.5, 128.8, 128.5, 122.3, 122.3, 115.8, 78.5, 55.4, 20.3; HRMS calcd for $C_{17}H_{16}ClNO$ 285.0920, found 285.0911.

*6-(4-Fluorophenyl)-4-methyl-2-phenyl-3,6-dihydro-2H-1,2-oxazine (**3c**):* pale yellow oil (72.3 mg, 87%); ^1H NMR (400 MHz, $CDCl_3$) δ 7.42−7.38 (dd, J = 8.8, 5.6 Hz, 2 H), 7.28−7.24 (m, 2 H), 7.08−7.00 (m, 4 H), 6.95 (t, J = 7.2 Hz, 1 H), 5.71 (s, 1 H), 5.49 (s, 1 H), 3.76 (AB quartets, J = 7.2 Hz, 2 H), 1.89 (s, 3 H); ^{13}C NMR (100 MHz $CDCl_3$) δ 150.1, 131.9, 130.0, 129.9, 128.8, 122.6, 122.2, 115.8, 115.3, 115.1, 78.6, 55.3, 20.3; HRMS calcd for $C_{17}H_{16}FNO$ 269.1216, found 269.1217.

*6-(4-Bromophenyl)-4-methyl-2-phenyl-3,6-dihydro-2H-1,2-oxazine (**3d**):* yellow oil (57.7 mg, 78%); ^1H NMR (400 MHz, $CDCl_3$) δ 7.47 (d, J = 8.4 Hz, 2 H), 7.31−7.24 (m, 4 H), 7.07 (d, J = 8.4 Hz, 2 H), 6.95 (t, J = 7.2 Hz, 1 H), 5.70 (s, 1 H), 5.46 (s, 1 H), 3.75 (AB quartets, J = 7.2 Hz, 2 H), 1.88(s, 3 H); ^{13}C NMR (100 MHz $CDCl_3$) δ 150.1, 138.6, 132.1, 131.5, 129.8, 128.8, 122.3, 122.2, 122.2, 115.8,

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78.5, 55.4, 20.3; HRMS calcd for $C_{17}H_{16}BrNO$ 329.0415, found 329.0410.

*4-Methyl-2-phenyl-6-(4-(trifluoromethyl)phenyl)-3,6-dihydro-2H-1,2-oxazine (**3e**):* yellow oil (45.2 mg, 60%); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.60−7.54 (m, 4 H), 7.28−7.26 (m, 2 H), 7.09 (d, J = 8.4 Hz, 2 H), 6.97 (t, J = 8.4 Hz, 1 H), 5.73 (s, 1 H), 5.55 (s, 1 H), 3.77 (AB quartets, J = 7.2 Hz, 2 H), 1.89 (s, 3 H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 150.1, 143.7.0, 132.3, 130.2 (q, J_{C-F} = 32.3 Hz), 128.8, 128.1, 125.3, 125.3, 122.4, 122.0, 115.9, 78.5, 55.6, 20.3; HRMS calcd for $C_{18}H_{16}F_3NO$ 319.1184, found 319.1180.

*4-Methyl-2-phenyl-6-(p-tolyl)-3,6-dihydro-2H-1,2-oxazine (**3f**):* yellow oil (70.4 mg, 84%); ^{1}H NMR (400 MHz $CDCl_3$) δ 7.34 (d, J = 7.6 Hz, 2 H), 7.26 (t, J = 8 Hz, 2 H), 7.18 (d, J = 8 Hz, 2 H), 7.11 (d, J = 8 Hz, 2 H), 6.95 (t, J = 7.6 Hz, 1 H), 5.74 (s, 1 H), 5.50 (s, 1 H), 3.77 (AB quartets, J = 7.2 Hz, 2 H), 2.34 (s, 3 H), 1.89 (s, 3 H); ^{13}C NMR (100 MHz $CDCl_3$) δ 150.3, 138.0, 136.5, 131.4, 129.1, 128.7, 128.1, 123.1, 122.0, 115.8, 79.11, 55.3, 21.2, 20.3; HRMS calcd for $C_{18}H_{19}NO$ 265.1467, found 265.1459.

*6-(4-Methoxyphenyl)-4-methyl-2-phenyl-3,6-dihydro-2H-1,2-oxazine (**3g**):* yellow oil (58.1 mg, 72%); ^{1}H NMR (400 MHz $CDCl_3$) δ 7.36 (d, J = 8.4 Hz, 2 H), 7.26−7.22 (m, 2 H), 7.09 (d, J = 8.4 Hz, 2 H), 6.93 (t, J = 6.0 Hz, 1 H), 6.89 (d, J = 8.8 Hz, 2 H), 5.72 (s, 1 H), 5.46 (s, 1 H), 3.79 (s, 3 H), 3.76−3.74 (AB quartets, J = 7.2 Hz, 2 H), 1.88 (s, 3 H); ^{13}C NMR (100 MHz $CDCl_3$) δ 159.6, 150.2, 131.7, 131.5, 129.6, 128.7, 123.1, 122.0, 115.8, 113.7, 78.9, 55.3, 55.2, 20.3; HRMS calcd for $C_{18}H_{19}NO_2$ 281.1416, found 281.1412.

*4-Methyl-6-(naphthalen-2-yl)-2-phenyl-3,6-dihydro-2H-1,2-oxazine (**3h**):* pale yellow oil (50.4 mg, 65%); ^{1}H NMR (400 MHz $CDCl_3$) δ 7.87 (s, 1 H), 7.85−7.81 (m, 3 H), 7.59 (d, J = 8.8 Hz, 1 H),7.47 (m, 2 H), 7.26 (t, J = 7.2 Hz, 2 H), 7.13 (d, J = 8.0 Hz, 2 H), 6.95 (t, J = 8.0 Hz, 1 H), 5.84 (s, 1 H), 5.69 (s, 1 H),3.82 (AB quartets, J = 7.2 Hz, 2 H), 1.91 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.2, 137.0, 133.3, 133.2, 131.8, 128.7, 128.1, 128.1, 127.6, 127.2, 126.1, 126.0, 125.9, 122.8, 122.1, 115.9, 79.4, 55.4, 20.4; HRMS calcd for $C_{21}H_{19}NO$ 301.1467, found 301.1469.

*6-(Benzo[d][1,3]dioxol-5-yl)-4-methyl-2-phenyl-3,6-dihydro-2H-1,2-oxazine (**3i**):* yellow oil (57.3 mg, 73%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28−7.25 (m, 2 H), 7.10 (d, J = 8.4 Hz, 2 H), 6.97−6.90 (m, 3 H), 6.94 (d, J = 8.0 Hz, 1 H), 5.94 (s, 2 H), 5.70 (s, 1 H), 5.43 (s, 1 H), 3.75 (AB quartets, J = 7.2 Hz, 2 H), 1.89 (s, 3 H); ^{13}C NMR (100 MHz $CDCl_3$) δ 150.2, 147.6, 147.5, 133.4, 131.8, 128.7, 122.9, 122.1, 122.0, 115.8, 108.7, 108.0, 101.03, 79.1, 55.2, 20.3; HRMS calcd for $C_{18}H_{17}NO_3$ 295.1208, found 295.1208.

*6-(Furan-3-yl)-4-methyl-2-phenyl-3,6-dihydro-2H-1,2-oxazine (**3j**):* yellow and brown oil (60.3 mg, 67%); ^{1}H NMR (400 MHz $CDCl_3$) δ 7.45 (s, 1 H), 7.38 (s, 1 H), 7.29−7.25 (m, 2 H), 7.10−7.08 (m, 2 H), 6.97 (t, J = 7.2 Hz, 1 H), 6.48 (s, 1 H), 5.72 (s, 1 H), 5.47 (s, 1 H), 3.72 (AB quartets, J = 7.2 Hz, 2 H),1.86 (s, 3 H); ^{13}C NMR (100 MHz $CDCl_3$) δ 150.2, 143.1, 140.8, 131.8, 128.8, 124.5, 122.1, 122.1, 115.8, 109.9, 71.9, 55.2, 20.2; HRMS calcd for $C_{15}H_{15}NO_2$ 241.1103, found 241.1106.

*6-(Furan-2-yl)-4-methyl-2-phenyl-3,6-dihydro-2H-1,2-oxazine (**3k**):* yellow and brown oil (62.1 mg, 69%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 (s, 1 H), 7.27 (t, J = 7.2 Hz, 2 H), 7.09 (d, J = 8.0 Hz, 2 H), 6.96 (t, J = 7.2 Hz, 1 H), 6.35−6.34 (d, J = 6.0 Hz, 2 H), 5.77 (s, 1 H), 5.53 (s, 1 H), 3.73 (AB quartets, J = 7.2 Hz, 2 H), 1.89 (s, 3 H); ^{13}C NMR (100 MHz $CDCl_3$) δ 152.8, 150.0, 142.8, 133.2, 128.7, 122.2, 119.6, 115.9, 110.3, 109.4, 72.4, 54.9, 20.3; HRMS calcd for $C_{15}H_{15}NO_2$ 241.1103, found 241.1105.

*4-Methyl-2-phenyl-6-(thiophene-2-yl)-3,6-dihydro-2H-1,2-oxazine (**3l**):* yellow and brown oil (57.3 mg, 67%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28−7.23 (m, 3 H), 7.09−7.07 (m, 3 H), 6.98−6.93 (m, 2 H), 5.81 (s, 1 H), 5.70(s, 1 H), 3.79−3.70 (m, 2 H), 1.88 (s, 3 H); ^{13}C NMR (100 MHz $CDCl_3$) δ 149.9, 143.0, 132.1, 128.7, 126.3, 126.3, 126.2, 122.3, 122.2, 115.9, 74 0.5, 55.0, 20.2; HRMS calcd for $C_{15}H_{15}NOS$ 257.0874, found 257.0876.

*2,4,6-Triphenyl-3,6-dihydro-2H-1,2-oxazine (**3m**):* pale yellow oil (68.4 mg, 90%); ^{1}H NMR (400 MHz $CDCl_3$) δ 7.5 (m, 4 H), 7.40−7.27 (m, 8 H), 7.19 (d, J = 8.6 Hz, 2 H), 6.99 (t, J = 7.2 Hz, 1 H), 6.39 (d, J = 1.6 Hz, 1 H), 5.73 (d, J = 2.4 Hz, 1 H), 4.36−4.22 (AB quartets, J = 7.2 Hz, 2 H); ^{13}C NMR (100 MHz $CDCl_3$) δ 150.2, 139.0, 138.0, 134.3, 128.8, 128.7, 128.5, 128.48, 128.3, 128.0, 125.1, 125.0, 122.5, 116.2, 79.6, 53.3; HRMS calcd for $C_{22}H_{19}NO$ 313.1467, found 313.1464.

*3-Methyl-2,4,6-triphenyl-3,6-dihydro-2H-1,2-oxazine (**3n**):* white solid (47.5 mg, 66%); melting point 144.5−146 °C; ^{1}H NMR (400 MHz $CDCl_3$) δ 7.50−7.47 (m, 4 H) 7.42 (t, J = 7.2 Hz, 2 H), 7.35−7.23 (m, 6 H), 7.09−7.06 (m, 2 H), 6.89 (t, J = 1.6 Hz, 1 H), 6.36 (d, J = 2.8 Hz, 1 H) 5.58 (d, J = 3.6 Hz, 1 H) 4.76−4.74 (m, 1 H),1.16 (d, J = 6.4 Hz, 3 H) ; ^{13}C NMR (100 MHz $CDCl_3$) δ 148.7, 141.2, 140.3, 138.1, 128.7, 128.7, 128.2, 128.0, 127.9, 127.8, 126.2, 123.5, 121.0, 115.7, 78.9, 55.9, 12.5; HRMS calcd for $C_{23}H_{21}NO$ 327.1623, found 327.1616.

*3-Methyl-2,4,6-triphenyl-3,6-dihydro-2H-1,2-oxazine (**3n′**):* pale yellow oil (18.6 mg, 25%); ^{1}H NMR (400 MHz $CDCl_3$) δ 7.50−7.36 (m, 9 H), 7.33−7.28 (m, 3 H), 7.17 (d, J = 7.6 Hz, 2 H), 6.95 (t, J = 7.6 Hz, 1 H), 6.12 (s, 1 H), 5.66 (s, 1 H), 4.79−4.75 (m, 1 H), 1.28 (d, J = 6.4 Hz, 3 H); ^{13}C NMR (100 MHz $CDCl_3$) δ 148.5, 140.4, 138.5, 137.9, 128.9, 128.7, 128.7, 128.6, 128.2, 128.0, 125.9, 125.2, 121.5, 115.9, 79.5, 55.8, 14.5; HRMS calcd for $C_{23}H_{21}NO$ 327.1623, found 327.1626.

*6-Methyl-2,4-diphenyl-3,6-dihydro-2H-1,2-oxazine (**3o**):* yellow oil (73.2 mg, 84%); ^{1}H NMR (400 MHz $CDCl_3$) δ 7.44 (d, J = 8.0 Hz, 2 H), 7.39−7.3 (m, 5 H), 7.23 (d, J = 8.0 Hz, 2 H), 7.03 (t, J = 7.6 Hz, 1 H), 6.19 (d, J = 2 Hz, 1 H), 4.86−4.84 (m, 1 H), 4.26−4.06 (AB quartets, J = 7.2 Hz, 2 H), 1.43 (d, J = 5.6 Hz, 3 H); ^{13}C NMR (100 MHz $CDCl_3$) δ 150.4, 139.2, 133.4, 128.8, 128.6, 127.8, 127.1, 125.0, 122.3, 116.0, 73.6, 53.2, 19.1; HRMS calcd for $C_{17}H_{17}NO$ 251.1310, found 251.1312.

*6-Ethyl-2,4-diphenyl-3,6-dihydro-2H-1,2-oxazine (**3p**):* yellow oil (57.8 mg, 69%); ^{1}H NMR (600 MHz $CDCl_3$) δ 7.43 (d, J = 8.4 Hz, 2 H), 7.36−7.27 (m, 5 H), 7.21 (d, J = 8.4 Hz, 2 H), 7.01 (t, J = 7.2 Hz, 1 H), 6.21 (s, 1 H),4.63−4.59 (m, 1 H), 4.25−4.06 (AB quartets, J = 7.2 Hz, 2 H), 1.82−1.69 (m, 2 H), 1.13 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz $CDCl_3$) δ 150.5, 138.3, 133.8, 128.9, 128.6, 127.8, 126.0, 125.0, 122.1, 115.8, 78.7, 53.4, 26.7, 10.1; HRMS calcd for $C_{18}H_{19}NO$ 265.1467, found 265.1457.

*2-Phenyl-6-propyl-5-(thiophene-2-yl)-3,6-dihydro-2H-1,2-oxazine (**5a**):* yellow oil (52.8 mg, 66%); ^{1}H NMR (600 MHz $CDCl_3$) δ 7.28−7.21 (m, 2 H), 7.20 (d, J = 1.2 Hz, 1 H), 7.07−6.93 (m, 4 H), 6.93 (s, 1 H), 5.98 (m, 1 H), 4.53−4.49 (m, 1 H), 4.39−4.24 (m, 1 H), 4.23−4.21 (m, 1 H), 2.02−1.70 (m, 2 H), 1.50−1.38 (m, 2 H) 0.86 (t, J = 7.4 Hz, 3 H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 148.0, 142.9, 132.6, 129.0, 127.5, 124.1, 122.1, 121.6, 119.7, 116.5, 63.6, 58.2, 34.3, 20.4, 14.1; HRMS calcd for $C_{17}H_{19}NOS$ 285.1187, found 285.1183.

*2-Phenyl-6-propyl-5-(thiophene-3-yl)-3,6-dihydro-2H-1,2-oxazine (**5b**):* yellow oil (50.4 mg, 63%); ^{1}H NMR (600 MHz $CDCl_3$) δ 7.32−7.31 (d, J = 3.0 Hz, H), 7.29−7.26 (m, 2 H), 7.21−7.19 (m, 2 H), 7.08 (dd, J = 8.4, 1.2 Hz, 2 H), 6.93 (t, J = 1.2 Hz, 1 H) 5.98−5.97 (m, 1 H), 4.55−4.39 (m, 1 H), 4.27 (m, 1 H), 4.26−4.23 (m, 1 H), 1.99−1.67 (m, 2 H), 1.55−1.37 (m, 2 H), 0.85 (t, J = 7.2 Hz, 3 H); ^{13}C NMR (150 MHz $CDCl_3$) δ 148.2, 140.2, 133.4, 129.0, 126.0, 125.0, 121.4, 119.7, 119.1, 116.4, 63.9, 58.0, 34.2, 20.4, 14.1; HRMS calcd for $C_{17}H_{19}NOS$ 285.1187, found 285.1185.

*4-Methyl-6-phenyl-2-(p-tolyl)-3,6-dihydro-2H-1,2-oxazine (**6a**):* yellow oil (65.4 mg, 71%); ^{1}H NMR (400 MHz $CDCl_3$) δ 7.44 (d, J = 8.4 Hz, 2 H), 7.37−7.30 (m, 3 H), 7.08−7.01 (m, 4 H), 5.74 (s, 1 H), 5.52 (s, 1 H), 3.73 (AB quartets, J = 7.2 Hz, 2 H), 2.27 (s, 3 H), 1.88 (s, 3 H); ^{13}C NMR (100 MHz $CDCl_3$) δ 148.0, 139.7, 131.7, 131.6, 129.3, 128.3, 128.1, 128.0, 122.9, 116.2, 79.2, 55.8, 20.6, 20.3; HRMS calcd for $C_{18}H_{19}NO$ 265.1467, found 265.1457.

*2-[4-(tert-Butyl)phenyl)]-4-methyl-6-phenyl-3,6-dihydro-2H-1,2-oxazine (**6b**).* yellow oil (77.8 mg, 73%); ^{1}H NMR (400 MHz $CDCl_3$) δ 7.44 (d, J = 7.2 Hz, 2 H), 7.36−7.27 (m, 5 H), 7.05 (d, J = 8.8 Hz, 2 H), 5.73 (s, 1 H), 5.51 (s, 1 H), 3.74 (AB quartets, J = 7.2 Hz, 2 H), 1.88 (s, 3 H), 1.27 (s, 9 H); ^{13}C NMR (100 MHz $CDCl_3$) δ 147.8, 145.1, 139.7, 131.6, 128.3, 128.1, 128.0, 125.5, 122.9, 115.9, 79.2, 55.6, 34.1, 31.9, 20.3; HRMS calcd for $C_{21}H_{25}NO$ 307.1936, found 307.1929.

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*2-(4-Chlorophenyl)-4-methyl-6-phenyl-3,6-dihydro-2H-1,2-oxazine (**6c**):* yellow and brown oil (80.3 mg, 81%); ^{1}H NMR (400 MHz $CDCl_3$) δ 7.42 (d, J = 7.6 Hz, 2H), 7.37−7.31 (m, 3H), 7.21 (d, J = 8.8 Hz, 2H), 7.02 (d, J = 8.8 Hz, 2H), 5.74 (s, 1 H), 5.51 (s, 1 H), 3.73 (AB quartets, J = 7.2 Hz, 2 H), 1.88 (s, 3 H); ^{13}C NMR (100 MHz $CDCl_3$) δ 148.8, 139.3, 131.3, 128.7, 128.4, 128.3, 128.0, 127.0, 122.9, 117.0 79.4, 55.2, 20.3; HRMS calcd for $C_{17}H_{16}ClNO$ 285.0920, found 285.0915.

*2-(4-Fluorophenyl)-4-methyl-6-phenyl-3,6-dihydro-2H-1,2-oxazine (**6d**):* yellow and brown oil (64.4 mg, 69%); ^{1}H NMR (400 MHz $CDCl_3$) δ 7.43 (d, J = 7.6 Hz, 2 H), 7.37−7.31 (m, 3 H), 7.08−7.05 (m, 2 H), 6.97−6.93 (m, 2 H), 5.74 (s, 1 H), 5.52 (s, 1 H), 3.71 (AB quartets, J = 7.2 Hz, 2 H), 1.88 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.6 (J_{C-F} = 239 Hz), 146.5 (J_{C-F} = 2 Hz), 139.4, 131.5, 128.4, 128.3, 128.0, 122.9, 117.8 (J_{C-F} = 8 Hz), 115.28 (J_{C-F} = 23 Hz), 79.5, 56.0, 20.3; HRMS calcd for $C_{17}H_{16}FNO$ 269.1216, found 269.1215.

■ ASSOCIATED CONTENT

Supporting Information

^{1}H, ^{13}C NMR and HRMS spectra of cycloadducts **3**, **5**, and **6**; crystallographic data for compound **3n** (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: rsliu@mx.nthu.edu.tw.

Notes

The authors declare no competing financial interest.

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